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ALP Program Report

2021 Fall - Cycle 46

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ALP Overview

Special points of interest:

- An assessment soil homogeneity indicate ALP reference soil materials were highly uniform for Cycle 46.
- Sixty-three Laboratories provided soil pH (1:1) H_2O results and medians ranged from 4.04 - 8.04.
- Soil M3-P ICP for Cycle 46 ranged from 10.6 to 78.6 mg kg^{-1} with MAD values ranging 1.0 - 5.4 mg kg^{-1} across the five soils.
- Soil M3-K values ranged from 96 - 357 mg kg^{-1} for the five ALP soils of PT Cycle 46.
- Botanical N by combustion was reported by 38 labs, with five labs showing high bias values on three of four botanical materials for Cycle 46.
- Botanical Total K, ranged from 0.63 - 7.13% with one lab noted for inconsistency across two of four samples.

Inside this issue:

The Agriculture Laboratory Proficiency (ALP) Program fall 2021 Round Cycle 46 was completed November 19, 2021, with results from one-hundred seven labs enrolled from the US, Canada, South Africa, Italy, Ukraine, Guatemala and Philippines. Proficiency samples consisted of five soils, four botanical and three water samples. Analytical methods are base on those published by AOAC, regional soil work groups, the Soil Plant Analysis Council and Forestry Canada. ALP has completed fifteen years of service to Ag laboratory industry.

Data was compiled for each method (test code) and proficiency material. Data analysis of each material include: the number results; grand median value; median absolute deviation (MAD), (95% Confidence Interval); method intra-lab standard deviation (*s*); lab mean, and standard deviation. Additional information on methods and statistical protocols can be found at the program web site.

Proficiency Materials

Standard Reference Soils (SRS) materials utilized for Cycle 46 were: SRS-2111 a Norte gravelly sandy loam, collected Rio Grande Cty, CO; SRS-2112 Darfur fine sandy loam collected Watonwan Cty, MN; SRS-2113 a Page loamy fine sand collected Garfield Cty, NE; SRS-2114 is a clay loam collected near Weyburn, SK, Canada; and SRS-2115 a Norge loam, collected Payne Cty, OK. Chemical properties of the SRS materials ranges: pH (1:1) 0.01 M $CaCl_2$ 3.82 - 7.74; SMP Buf 6.53 - 7.50 mg kg^{-1}; Bray P1 (1:10) 2.3 - 58.2 mg kg^{-1}; M3-K 96 - 357 mg kg^{-1}; M3-Ca 400 - 6746 mg kg^{-1}; DTPA-Zn 0.36 - 2.33 mg kg^{-1}; SOM-LOI 1.32 – 3.44%; CEC 5.1 - 23.6 cmol kg^{-1}; clay 7.0 - 38.4 % and total P 152 - 910 mg kg^{-1}.

Standard Reference Botanical (SRB) materials for Cycle 46 were: SRB-2109 olive leaf composite from CA; SRB-2110 buckwheat leaf composite from CO; SRB-2111 soybean leaf composite from AR; and SRB-2112 canola leaf composite from IA. SRB median analytes ranged: NO_3-N 22 - 6249 mg kg^{-1}; Dumas N 1.46 - 6.23%; total P 0.098 - 0.664%; K 0.64 - 6.98%; Ca 0.99 - 2.13%; S 0.13 - 0.84 %, B 15.7 - 49.7 mg kg^{-1}; and Mo 0.13 - 5.1 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-2107 a water sample collected from a James River, South Dakota: SRW-2108 was collected from a domestic well Sioux Center, IA; and SRW-2109 an artificial water sample. SRW median concentrations range: pH 7.83 - 7.91; EC 0.21 - 0.31 dSm^{-1}; SAR 0.21 - 0.46; Ca 0.52 - 1.99 mmolc L^{-1}; Na 0.12 - 0.51 mmolc L^{-1}; SO_4 0.06 - 0.71 mmolc L^{-1}; and Cl 0.08 - 14.2 mmolc L^{-1}.

Soil Homogeneity Evaluation

SRS material homogeneity was evaluated based on soil test codes pH (1:1) H_2O, buffer pH Adams Evans, EC (1:1), P Olsen, K Olsen, NO_3-N and SOM-WB on analysis of five jars of each PT soil, each in analyzed in triplicate by an independent laboratory. Homogeneity results were within acceptable limits for all soils, with the lowest noted for pH H_2O. Homogeneity was also evaluated on SRB and SRW matrix sam-

"..soil pH, Buf pH A&E, Olsen P and SOM-WB analysis Stdev values for Cycle 46 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation 2021, Cycle 46.

Sample	pH (1:1) H_2O		EC (1:1) (dS m^{-1})		Olsen P (mg kg^{-1})		SOM-WB (%)	
	Mean [1]	*Std*	Mean	*Std*	Mean	*Std*	Mean	*Std*
SRS-2111	6.14	*0.03*	0.98	*0.017*	17.4	*0.5*	2.16	*0.08*
SRS-2112	7.92	*0.01*	0.25	*0.021*	3.1	*0.2*	3.04	*0.10*
SRS-2113	4.00	*0.02*	0.86	*0.006*	30.4	*0.9*	1.41	*0.06*
SRS-2114	7.91	*0.02*	1.21	*0.008*	15.0	*0.4*	1.69	*0.11*
SRS-2115	5.62	*0.02*	0.21	*0.012*	3.5	*0.6*	1.32	*0.06*

[1] Statistics based on six randomly selected soil replicates, each analyzed in triplicate ALP Cycle 46.

2021 Cycle 46 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis inter-lab MAD values for Cycle 46 averaged 0.06 pH units across the five soils. Median within lab pH standard deviation was 0.05 pH units. SRS-2113 had an abnormally low extractable M3-Mg of 69 mg kg^{-1}, likely associated with the Page loamy sand soil series. Soil organic C values for the cycle 46 ranged form 0.65 to 2.19% SOC. Soil M3-Ca (Test code 160) inter-lab MAD values ranged 50 - 552 mg kg^{-1} and M3-Mg MAD values ranged 7.4 to 54 mg kg^{-1} for the five soils. Across soils M3-P colorimetric within lab standard deviations were ranged from 0.32 - 1.3 mg kg^{-1}. Soil SRS-2115 had abnormally low M3-Zn and DTPA-Zn, 0.64 and 0.35 mg kg^{-1}, respectively. The soil site collection meta shows the loam soil was collected from an field research site near Stillwater, Oklahoma.

Across the four botanical samples Dumas combustion N MAD values averaged 0.049% nitrogen with intra-lab median *s* of 0.035%, 0.055%, 0.060% and 0.158, respectively. Botanical sample SRB-2112 had a high median S with a concentration of 0.84 % and with a MAD of 0.058 %. Botanical sample SRB-2112, the canola sample composite, had elevated extractable Cl 1.24%. It also had higher median concentrations of NO_3-N, PO_4-P, K, Mo, Ba, and Cd and relative to the other three botanical samples. Consistent with past ALP cycles for 2021, cycle 46 general intra-lab relative variability results were lowest for combustion N than other macro elements across all four botanical samples.

Water EC results showed high consistency across samples. Across the three water samples EC Median values ranged from 0.31, 0.21 and 5.60 dSm^{-1}, respectively. Ca mean concentrations ranged from 0.52 - 2.00 molc L^{-1} across the three ALP cycle 46 water samples with MAD values ranging 0.054 to 0.108 molc L^{-1}. Sample SRW-2109 had Cl of 14.2 with a MAD of 0.97.

SRS - pH (1:1)$_{H2O}$

Sixty-three laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 4.04 - 8.04. Lab results were ranked low to high based on sample SRS-2113 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-2111 and SRS-2112 showed good consistency across labs. Lab #1 showed consistent low bias on all five samples. Labs #6, #7, #21, #26, #62 and #63 were inconsistent on high pH soils relative to SRS-2113. Source of bias is associated with ISE performance and/or method compliance. Inconsistency could be result of extract carry-over.

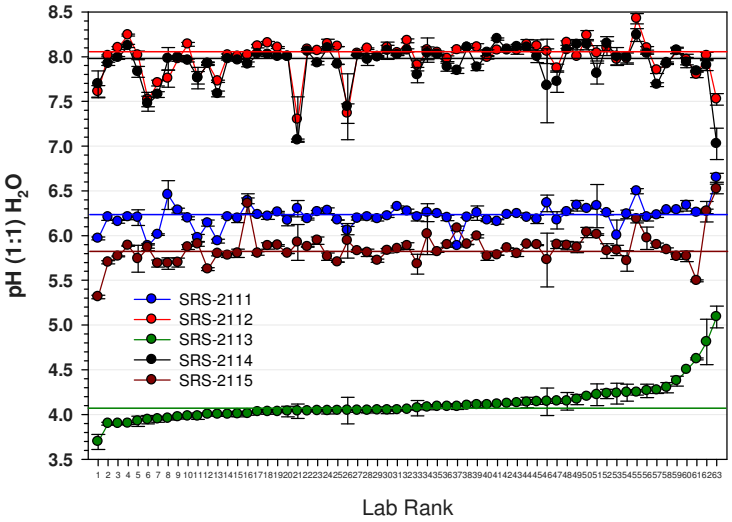


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2021 Cycle 46.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.026 to 0.031 pH units, the lowest noted for SRS-2111. Thirteen labs had poor precisions, with standard deviations exceeding consensus median intra-lab *s*. Specifically *s* for labs #8, #51, #53, and #62 exceeded 0.10 pH units for SRS-2111. Soil SRS-2113 was the least variable with respect to intra-lab variance.

SRS - Phosphorus: Bray P1, Bray P2, Olsen, Modified Morgan, M1, and M3

Bray P1 results were reported by twenty-seven labs. M3-P ICP was reported by 40 labs. Median soil Bray P1 values ranged from 2.3 - 58.7 mg kg^{-1} PO_4-P; Olsen P 4.0 to 32.3 mg kg^{-1} P; M3-P ICP 10.6 - 78.6 mg kg^{-1} P; Bray P2 ranged from 12 to 106 mg kg^{-1} P; and M1-P from 2.7 to 78 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-2115, median M3-P ICP concentrations are shown in indicated in Figure 2. Soil SRS-2114 PO concentrations were highly variable between labs. Soils SRS-2112 and SRS-2115 had similar concentrations of 14.9 mg kg^{-1} and 10.6 mg kg^{-1} M3-P ICP. Lab #40 had consistently high bias across all five soils. Labs #8 and #30 were inconsistent for SRS-2111 relative to SRS-2115.

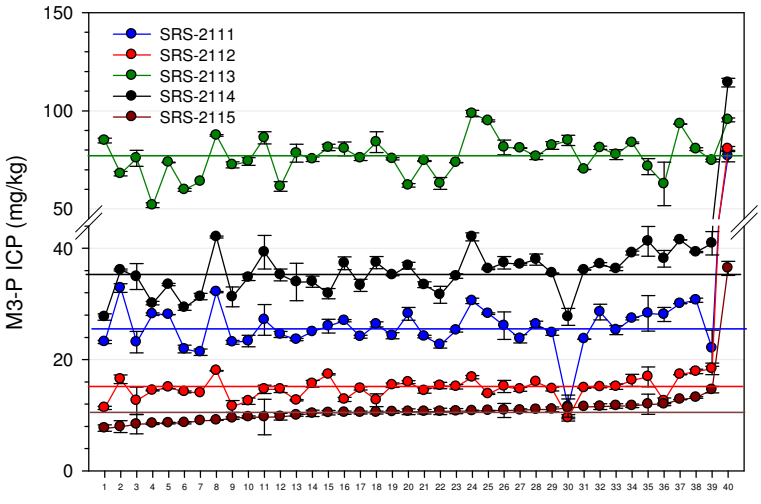


Figure 2. M3-P ICP distribution plots for SRS materials, ALP 2021 Cycle 46.

Seven labs reported M3-P spec median concentrations ranging 8.4 - 55 mg kg^{-1} PO_4-P for ALP cycle 46. Two labs reported results for Modified Morgan P, with medians for the five soils ranging from 1.2 - 13.3 mg kg^{-1} PO_4-P. Modified Kewlona was reported by two laboratories ranging from 4.9 - 28.9 mg kg^{-1} P for the five soils and total P (US-EPA 503) ranged 151 - 910 mg kg^{-1} P with the highest concentration noted for SRS-2111.

SRS - Potassium

Forty laboratories provided ALP results for soil M-3 K (test code 159) results. Results were ranked low to high based on sample SRS-2112 (see Figure 3). Soil SRS-2111 was the most inconsistent across all labs. The source of the variability is unknown. Labs #14 #25 and #39 were inconsistent across the four soils relative to SRB-2112. Source of inconsistency is likely related to sample extraction, analysis instrument and/or method compliance.

M3-K intra-lab *s* values were lowest for soil SRS-2112 with a median intra-lab value of 3.9 mg kg^{-1} for SRS-2109 and highest for SRS-2114 with a value of 14.2 mg kg^{-1}. M3-K within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 400 mg kg^{-1} K. Precision was poor (based on intra-lab *s*) for four labs which exceeded 20 mg kg^{-1} K on SRS-2111. Labs #11, #14, #33 and #43 had poor precision on two of four soils for cycle 46. Poor precision is attributed to extraction and/or analysis instrument operation.

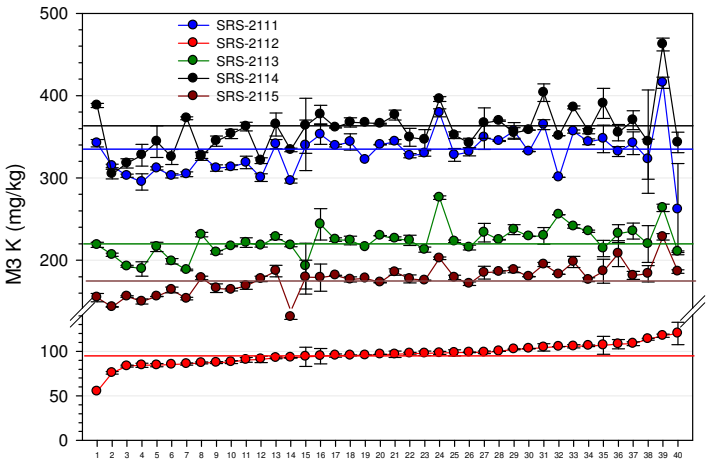


Figure 3. Extractable K distribution plots for SRS materials, ALP 2021 Cycle 46.

SRS - SOM-LOI

Forty-seven laboratories provided ALP results for soil SOM-LOI (test code 183). Soil Median SOM-LOI values ranged from 1.32 to 3.34%. Results were ranked based on sample SRS-2113 (see Figure 4). Sample SRS-2111 and SRS-2112 had high consistency. Labs #6, #12, #44 and #46 had inconsistency across all four soils relative to SRS-2113. Labs #6 and #44 had low bias on two soils. Source of bias is likely related to muffle furnace operation and/or method compliance.

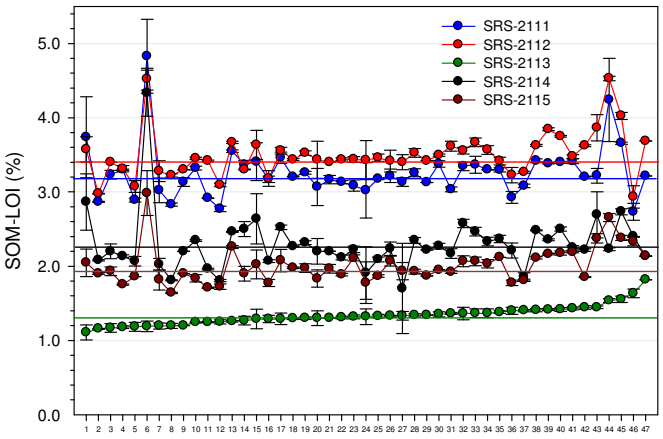


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2021 Cycle 46.

SOM-LOI precision across the five soils indicates high intra-lab precision, with median *s* values ranging from 0.055 to 0.120% SOM-LOI, highest for SRS-2112. Across labs, *s* values for SRS-2115 ranged from 0.006 - 0.30%. Across soils low precision was noted for several laboratories. Specifically *s* for labs #1, #15, #20, #24 and #43, exceeded 0.15% SOM-LOI for SRS-2112. Lab #24 had poor precision on four of five soils. Poor precision may be associated with muffle furnace crucible position and furnace heating.

SRS - DTPA-Cu

Forty-three laboratories provided ALP results for soil DTPA-Cu (test code 173). Results were ranked low to high based on sample SRS-2113 lowest in concentration (see Figure 5). Concentrations of DTPA-Cu for soil SRS-2114 were generally the most consistent across labs, whereas lab concentrations for soil SRS-2112 were more inconsistent across labs. Labs #40, #41 and #42 generally had high bias on soils containing less than 1.0 mg kg^{-1} DTPA extractable Cu. Labs #35 - #39 indicated high bias on soils low in DTPA-Cu. Across soils, lab #1 was inconsistent. Source of this inconsistency is likely related to instrument calibration or method compliance.

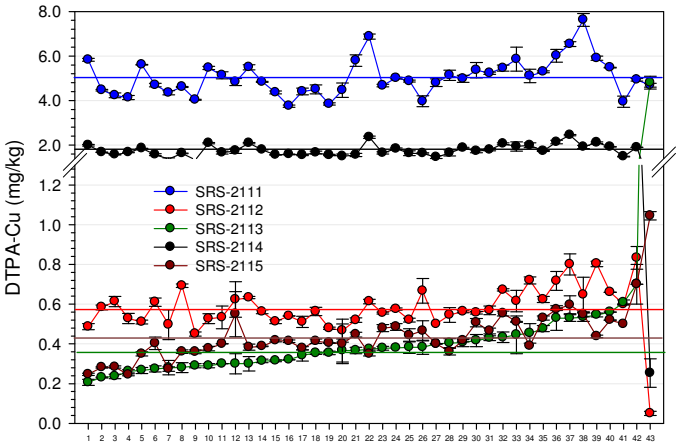


Figure 5. Comparison of soil DTPA-Cu distributions, Cycle 46.

Soil DTPA-Cu median intra-lab *s* values were lowest for ALP soil SRS-2112, averaging 0.04 mg kg^{-1} and highest for SRS-2111 with a value of 0.18 mg kg^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception labs #26 and # 38 for DTPA-Cu, > 0.06 mg kg^{-1} for soil SRS-2112. Eight labs were flagged for poor precision across the five soils.

SRB - NO_3-N

Seventeen laboratories provided ALP results for NO_3-N by cadmium reduction (test code 202). Median values are designated by horizontal lines for each of the four botanical materials used and labs results are ranked low to high for sample SRB-2109 (see Figure 6). The data plot shows a high degree of consistency for all four plots with bias noted for labs #5 and #14 for SRB-2110 and SRB-2112, respectively.

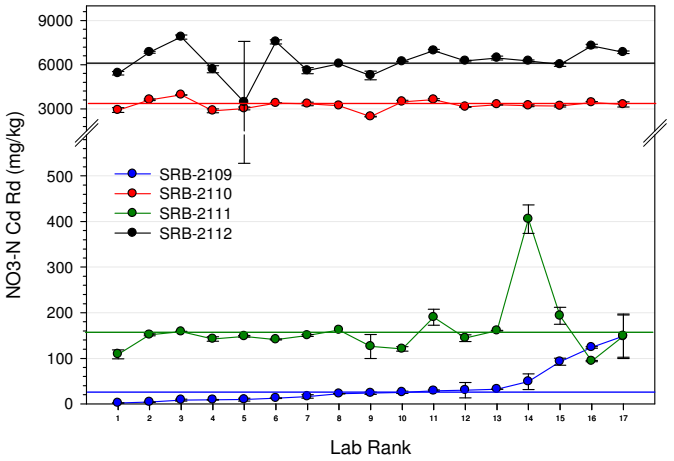


Figure 6. Nitrate distribution plots for SRB materials, ALP 2021, Cycle 46.

Botanical NO_3-N (test code 202) results for cycle 46 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 7.0 to 146 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction intra-lab *s* values for SRB-2109 ranged from 0.3 – 3.3 mg kg^{-1}; SRB-2110 ranged from 12 - 171 mg kg^{-1}, SRB-2111 ranged from 0.5 – 46 mg kg^{-1} and SRB-2112 ranged from 25 - 4130 mg kg^{-1}. Lab #5 had a consistently high standard deviation for SRB-2112 and Lab #17 for SRB-2109. Nine labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Thirty-eight laboratories provided ALP results for botanical Dumas (Combustion) nitrogen (test code 210) and nine labs for TKN (Test code 209) for Cycle 46. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-2112 (see Figure 7). Labs #2, #37 and #38 were inconsistent for SRB-2110 and SRB-2111 relative to SRB-2112. It is note worthy that TKN was inconsistent and lower than Dumas across three of four samples.

Dumas N results indicate very high precision across all labs for all samples. Individual lab Dumas N lab *s* values for SRB-2109, ranged 0.002 to 0.110% N, SRB-2110 ranged from 0.005 to 0.184% N, SRB-2111 ranged from 0.006 to 0.183 % N, and SRB–2112 from 0.005 to 0.969 % N. Lab #37 had consistently high standard deviations for SRB-2112. Lab TKN *s* values for SRB-2109 ranged from 0.003 to 0.069%, SRB-2110 ranged from 0.005 to 0.117% TKN, SRB-2111 ranged from 0.012 to 0.535% TKN nitrogen and SRB-2112 ranged from 0.015 to 0.278% TKN nitrogen.

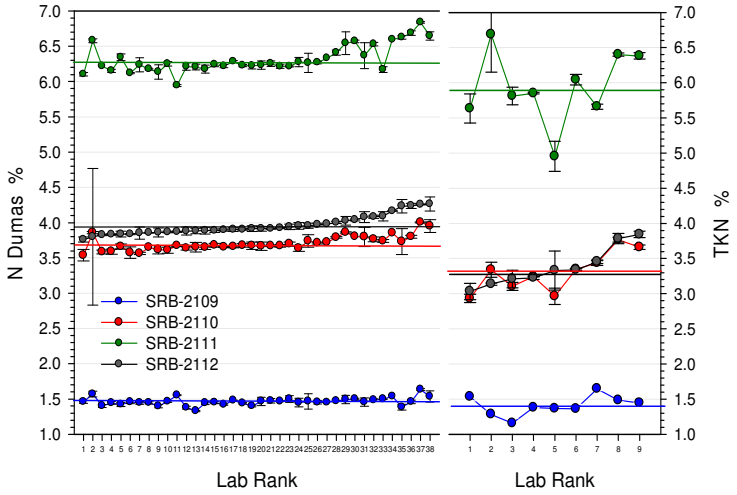


Figure 7. N distribution lab plots for SRB materials, ALP 2021 Cycle 46.

SRB - Phosphorus

Forty-six laboratories provided ALP results for Cycle 46 phosphorus (P) (test code 212). Botanical results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-2110 (see Figure 8). Labs #4, #8, #34, #27 and #44 showed inconsistency for SRB-2110 and SRB-2111 relative to SRB-2110. Source of inconsistency is likely related to sample extraction, analysis instrument and/or method compliance.

Botanical P results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged 0.004% to 0.025% P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-2109; ranged from 0.001 - 0.010 % P; SRB-2110 ranged from 0.001 – 0.052 % P and SRB-2111 0.001 - 0.055 % P; and SRB-2112 0.001 - 0.084 % P. Lab #42 had a high standard deviation exceeding 0.06 % P on SRB-2110 and SRB-2112 PT samples. Seven labs were flagged for poor precision for botanical P for Cycle 46.

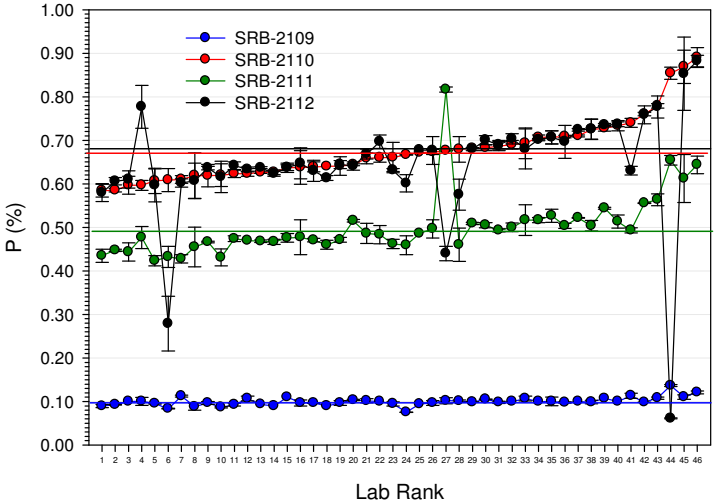


Figure 8. Phosphorus distribution lab plot for SRB materials, ALP 2021 Cycle 46.

SRB - Potassium

Forty-six laboratories provided ALP results for potassium (K) (test code 213). Median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-2111 (see Figure 9). Lab #9, #37 and #46 was inconsistent for SRB-2112 relative to SRB-2111. Low bias was noted for lab #1 for three of four PT samples. Source of bias is related sample digestion, analysis instrument and/or method compliance.

Botanical K results indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 0.025 to 0.250 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-2109, ranged from 0.002 - 0.120 % K; SRB-2110, 0.006 - 0.660 % K; SRB-2111, 0.006 - 0.208 % K; and SRS-2112, 0.004 - 1.74 % K. Lab #37 had high standard deviations exceeding 0.50 %K on two of four samples. Seven labs were flagged for poor K precision for Cycle 46.

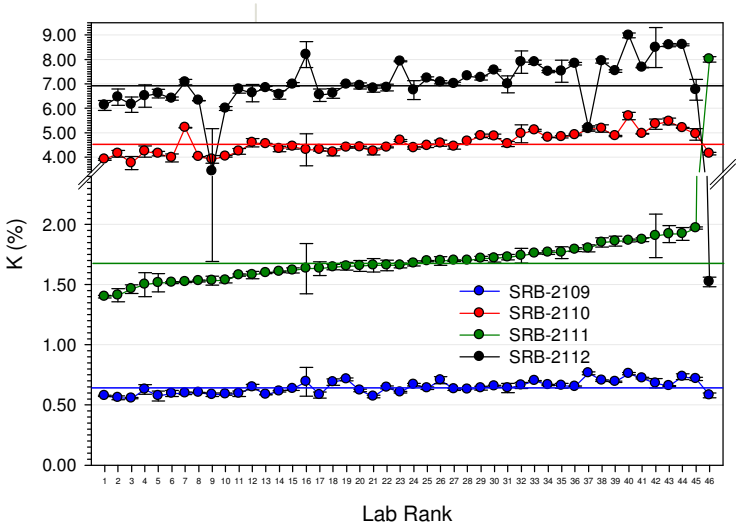


Figure 9. Potassium lab plot for SRB materials, ALP 2021 Cycle 46.

SRB - Boron

Forty-one laboratories provided ALP results for manganese (B) (test code 219). Result median values are designated by horizontal lines for each botanical material and individual labs results are ranked low to high based on sample SRB-2109 (see Figure 10). Across samples labs #1 and #2 exhibited low bias. Labs #12, #31, #32 and #41 were inconsistent relative to SRB-2109. Source of bias is related sample digestion, analysis instrument and/or method compliance.

Botanical B results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 0.9 to 3.0 mg kg^{-1} B for across the four botanical samples. Individual lab intra-lab *s* values for SRB-2109; ranged from 0.03 - 3.3 mg kg^{-1} B; SRB-2110 ranged from 0.07 – 2.3 mg kg^{-1} B; SRB-2111 0.01 - 4.5 mg kg^{-1} B; and SRB-2112 0.06 - 18 mg kg^{-1} B. Lab #2 and #31 had consistently high standard deviations for two samples. Six labs were flagged for poor B precision for Cycle 46.

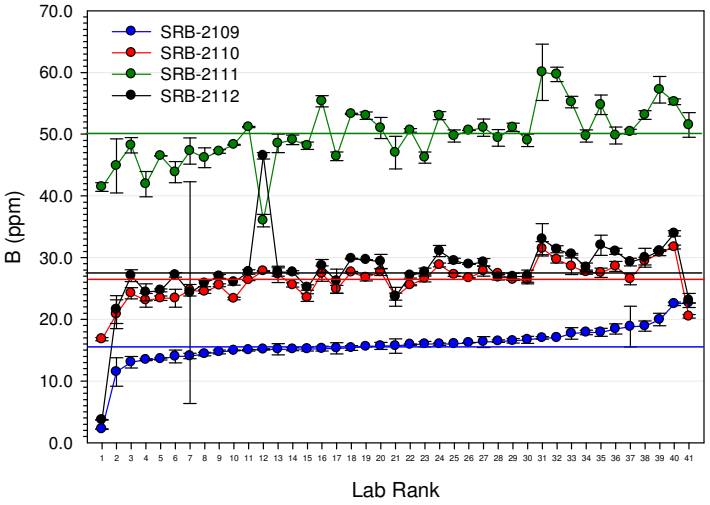
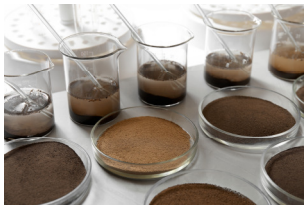


Figure 10. Boron lab plots for SRB materials, ALP 2021 Cycle 46.

SRW - Water EC



Eighteen laboratories provided ALP results for water EC (test code 302). Lab result were ranked low to high based on sample SRW-2108 (see Figure 11). Sample SRW-2109 had the highest EC in Cycle 46. Labs #18 indicated consistent high bias on all samples. Lab #1 had low bias on SRW-2107. Source of bias is likely associated with EC probe performance and/or calibration.

EC precision across the three water materials indicates very high precision, with intra-lab median Std values of 0.006, 0.004 and 0.099 dSm^{-1}, across the three samples respectively. Precision for sample SRW-2108 was the most consistent across the eighteen participating laboratories. Intra-lab s values for lab #18 exceeded 0.016 dSm^{-1} on SRW-2107. Highest precision was noted for lab #15 with intra-lab s values of < than 0.009 dSm^{-1} for all three samples.

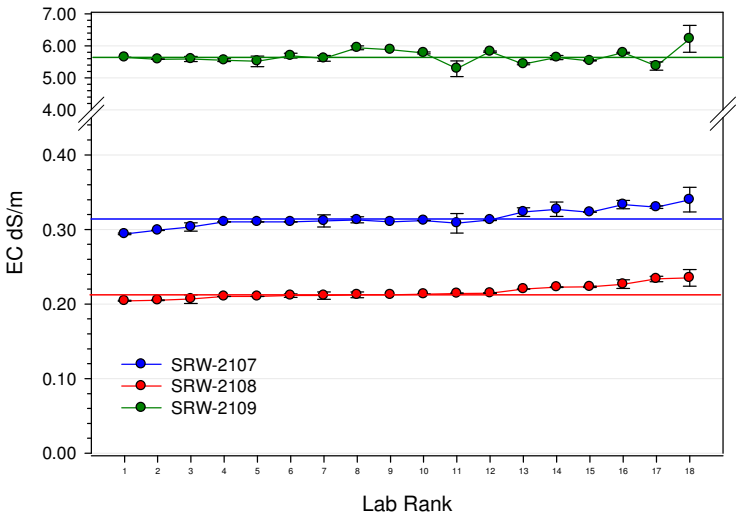


Figure 11 . Water EC distribution plots for SRW materials, ALP 2021 Cycle 46.

SRW - Ca Results

Eighteen laboratories provided ALP results for water Ca (test code 303). Lab results were ranked low to high based on sample SRW-2109 (see Figure 12) lowest in Ca concentration. Median values are designated by horizontal lines. For samples SRW-2107 and SRW-2108 lab results paralleled each other, likely associated with different instrument calibration curves amongst the eighteen labs. Lab #1 showed consistent low bias on all thee samples, and is likely a result of a calibration error.

Ca precision across the three water solution matrices indicates excellent precision, with intra-lab s values of 0.013, 0.008, and 0.010 meq L^{-1} for SRW-2107, SRW-2108, and for SRW-2109, respectively. Three labs were flagged for poor precision on ALP Cycle 46 for Ca content.

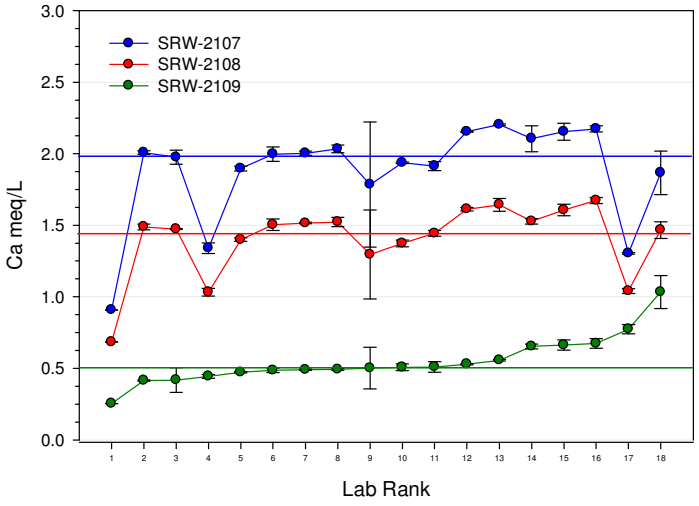


Figure 12. Water Ca distribution plots for SRW materials, ALP 2021 Cycle 46.

Announcements

- The Soil and Plant Analysis Council has launched a new web site, www.sp-council.org. The site includes information on the SPAC board, current projects and sales of soil scoops.
- The Soil and Plant Analysis Council (SPAC) and Agricultural Laboratory Testing Association (ALTA) have developed an international Plant Analysis Certification (PAC) program for laboratories. Analyses include: N, P, K, S, Ca, Mg, Zn, B, Mn, Fe, and Cu. The PAC program is based on ALP proficiency testing data evaluated on a yearly basis. More information can be found at ALTA.Ag.
- The Agricultural Laboratory Testing Association (ALTA) and SPAC are presenting a webinar "*Soil Scooping - Techniques*", January 18, 2022. For more information contact the ALTA secretary, gfisher@unitedsoilsinc.com.
- ALTA will have their 2022 winter meeting February 24-25, 2022 in Lafayette, Indiana. Topics include presentations on lab management; soil health; and ALTA-SAC certification.
- ALP has standard reference soils and plant tissue samples available for purchase in quantities of 0.2 - 20 kg. For more information on these methods contact the ALP Technical Director, Robert.Miller@cts-interlab.com.

Summary

ALP is has provided sixteen years of service with the completion of Cycle 46. Since 2005 ALP has completed the analysis of 230 soils, 148 plant samples and 131 water samples providing comprehensive proficiency data on inter and intra laboratory performance across a range of analytical methods.

We thank all laboratories who participated in Cycle 46. As the coordinators of the program we appreciate your consideration and participation in the proficiency program. We continually seek feedback from laboratory participants to improve the service and function of the program. Please forward all comments to info@cts-interlab.com.

Cycle 47 Ship

March 17, 2022

"a mistake repeated more than once is a decision."

– Paul Coelho, 1988

ALP
Agricultural Laboratory Proficiency Program